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RAINBOW SCATTERING IN INELASTIC MOLECULAR COLLISIONS

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## I. INTRODUCTION

The role of rainbow scattering in elastic collisions of atoms and atomic ions is well known[1,2] and provides an important link between experimental observation and the theoretical potential energy curve which governs the dynamics of the colliding atoms. Only recently, however, has the analogous phenomenon in the case of non-spherical potentials and inelastic collisions been investigated. Based on a comparison between a classical trajectory calculation and experiment it was suggested[3] that rainbow-like structures might be observable in the distribution of differential cross sections vs. the (quantized) rotational angular momentum of a diatomic molecule after collision with an atom or atomic ion. Several experiments have subsequently revealed such structure[4-10]. In the past two years numerous papers, experimental and theoretical, have appeared which discuss the subject[4-23]. Different researchers have, however, arrived at different and sometimes conflicting terminologies and interpretations of the theoretical analysis. Indeed, it has even been questioned whether the rainbow analogy is proper in this case. It is therefore appropriate to begin with a brief history of the main physical and mathematical concepts in rainbow scattering. This will be followed by a classical analysis of coplanar scattering of  $\text{Li}^+ + \text{CO}$ . Finally, a brief review of the experimental and theoretical literature is given.

## II. HISTORY

The rainbow is one of nature's most spectacular events, and it is therefore not too surprising that it has a long history of physical explanations. Aristotle (384-322 B.C.) apparently made the first recorded attempt [24] (ref. 24 is an exhaustive history of man's recorded thoughts on the rainbow.) Although in the intervening centuries there were several who correctly ascribed it to one reflection and two refractions of sunlight in the individual raindrops [24,25], it was Descartes in 1637 [26] who gave the first quantitative theoretical treatment. Using Snell's law for the index of refraction, which he may or may not have learned from Snell's work [27], he was able, by computing many light trajectories through a single water drop, to show that there was a minimum in the deflection angle and that at this angle the intensity of scattered light has its maximum.

Fig. 1(a) illustrates the scattering of light in a plane, through a spherical water drop of unit radius. A ray of light enters the drop from the right at  $P_1$  with an angle of incidence,  $\alpha$ , or impact parameter,  $b = \sin \alpha$ . It is refracted once, with refraction angle,  $\beta$ , then reflected at  $P_2$  and then refracted once again at  $P_3$ . The ray is deflected by an angle  $(\alpha - \beta)$  at  $P_1$ ,  $(\pi - 2\beta)$  at  $P_2$  and  $(\alpha - \beta)$  again at  $P_3$ . Therefore the total deflection angle is

$$\theta = \pi + 2\alpha - 4\beta \quad (1)$$

Using Snell's law

$$\sin \alpha = \mu \sin \beta \quad (2)$$

and a mean value of  $n = 1.333$  for the index of refraction of water in air, one can easily calculate the deflection angle  $\theta$  for any impact parameter,  $b$ . It can be seen in fig. 1(b) that  $\theta$  has a minimum value in the vicinity of  $\theta_m = 137.92^\circ$ . Furthermore, if one were to compute the trajectories for many such rays, evenly distributed over the impact parameter, one would find the distribution of deflected rays to be most concentrated around the minimum angle. In this way Descartes deduced that the rainbow should appear at the minimum angle. Using slightly more modern methods of analysis, one finds that for light scattered into a thin annular solid angle of  $2\pi \sin\theta d\theta$ , the relative intensity,  $I(\theta)$ , is given by,

$$I(\theta) = \sum_{i=1}^2 \frac{b_i}{\sin\theta} \left| \frac{db_i}{d\theta} \right| \quad (3)$$

where  $b_1$  and  $b_2$  are the two single-valued branches of the function  $b(\theta)$ . At  $\theta_m$  these two branches coalesce and the derivatives diverge, showing that the intensity of scattered light is a maximum. This is illustrated in fig. 1(c).

Furthermore, if one repeats this analysis for light rays which enter the lower half of the sphere and are reflected not once, but twice before emerging, one finds a maximum deflection angle of  $129.08^\circ$ . These angles are in excellent agreement with the angles at which the primary and secondary rainbows are observed.

Descartes' analysis was a remarkable feat, but was deficient in two main respects. It said nothing about the colors of the rainbow nor about

the supernumerary rainbows which sometimes appear faintly in the interior of the primary bow and on the exterior of the secondary bow. Newton resolved the problem of the colors[28], but the supernumerary rainbows are a wave interference effect and their explanation came more than 100 years later.

The complete problem of the scattering of light waves from water drops is quite complicated. However, in a famous work, the British astronomer Airy[29] gave an approximate solution to the problem which succeeded in resolving most of the remaining mysteries of the rainbow. Airy derived the expression for the intensity of scattered light,

$$I(\theta) = \left[ \int_0^{\infty} \cos 2\pi(\omega^3 - m\omega) d\omega \right]^2 \quad (4)$$

where  $m$  is proportional to  $\theta_A - \theta$ , the deviation from the rainbow angle, and depends on the drop's radius and the wavelength of the light. The integral in this expression is now commonly referred to as an Airy function. In some optics textbooks, however, one sees it referred to as the Airy rainbow integral[30,31].

Airy's equation gives an intensity which oscillates about the geometrical result, having its strongest peak just before the rainbow angle and decaying exponentially beyond it. This is illustrated in fig. 2. The weaker peaks describe quite accurately the positions and intensities of the supernumerary rainbows and the dependence of the intensity on the radius and wavelength resolves several other problems associated with the description of the rainbow[31].

fig 2

Let us now turn to the problem of elastic scattering of atoms. The classical and semiclassical treatments of this problem have been amply reviewed[1] and only selected aspects of them will be mentioned here. Fig. 3(a) shows the trajectories of two colliding atoms in the center-of-mass frame of reference. The deflection angle is a function of the impact parameter, and if the potential energy function has an attractive well, the function will look qualitatively like that in fig. 3(b). In fig. 3,  $\theta$  is the observation angle, which is the absolute value of the classical deflection function. The relative scattering intensity or differential cross section,  $\sigma(\theta)$ , is given by[32],

$$\sigma(\theta) = \sum_{i=1}^3 \frac{b_i}{\sin \theta} \left| \frac{db_i}{d\theta} \right| \quad (5)$$

the sum being over the three single-valued branches of  $b(\theta)$ . This is illustrated by the solid curve in fig. 3(c). The presence of an attractive well in the potential causes a maximum in  $\theta$  vs.  $b$ , and a singularity in the differential cross section. This is entirely analogous to the scattering of light from water drops, and hence has been called rainbow scattering[33]. The results of an early crossed atomic beam experiment[34] with K and Hg are reproduced in fig. 4. Allowing for the finite resolution of the apparatus, the cross sections in fig. 4 are very much what one would expect from classical mechanics.

Ford and Wheeler[33] in their semiclassical treatment of quantum mechanical rainbow scattering remark that the necessary mathematics is not essentially different from Airy's treatment of the reflection and

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refraction of light. Indeed, their semiclassical formula for the cross section contains the Airy function or rainbow integral. The semiclassical cross section is illustrated schematically in fig. 3(c). The need for such an analysis in atom-atom collisions is shown by the Na - Hg cross section measurements of Buck and Pauly[35], reproduced here in fig. 5. In this experiment the supernumerary rainbows are clearly resolved.

The problem of atoms colliding with molecules is in practice considerably more complicated due to the additional degrees of freedom. The simplest example is to approximate a diatomic molecule as a rigid linear rotor and consider collisions with a spherically symmetric atom (S electronic state.) In this case the classical cross section is given by,

$$\sigma(j', \theta) = \int_0^{2\pi} d\alpha \int_0^\pi \sin\beta d\beta \sum_i \frac{b_i}{4\pi \sin\theta} \left| \frac{\partial(b_i, \gamma_i)}{\partial(j', \theta)} \right| \quad (6)$$

where  $b$  is the impact parameter,  $\gamma$  is the initial angle of orientation of the rotor,  $j'$  is the final angular momentum of the rotor, and  $\theta$  is the scattering angle. (A detailed discussion of this formula and the other variables in it is given in the next section.) Instead of a simple derivative, as in eq. 5, this expression contains a Jacobian determinant of the partial derivatives of the two initial trajectory variables  $b$  and  $\gamma$  with respect to the final trajectory variables  $j'$  and  $\theta$ . The Jacobian, like the simple derivative in eq. 5, can be and often is singular. The analogy of this to rainbow scattering in the simpler spherically symmetric case is apparent and was recognized in early

semiclassical treatments of this problem[36,37]. In fact, it is the singularities of this Jacobian which necessitated the development of the "uniform" semiclassical theories (for a review and extensive references to the semiclassical literature, see ref. 38.) The differential cross section in eq. 6 is a function of both  $j'$  and  $\theta$ . Therefore, if the Jacobian is singular at a specific point ( $j'_A, \theta_A$ ), the rainbow-like structure will appear in both the angular distribution,  $\sigma(j'_A, \theta)$  vs.  $\theta$ , and the rotational state distribution,  $\sigma(j', \theta_A)$  vs.  $j'$ . Although the analogy to rainbow scattering in this case has been clearly understood[36,37] and observed in at least one classical trajectory calculation[39], prior to 1977 there was no discussion in the literature to suggest that rainbow structures might actually be observable in any distribution other than the angular distribution. This is probably due to the fact that in a quantum mechanical description, the momentum variables are quantized, and in the early quantal studies, primarily vibrational excitations and rotational excitations of  $H_2$  were considered. The energy spacings between adjacent quantum numbers are fairly large in these cases and no remnant of the classical singularities is obvious. However, considering again rotational excitation of a rigid-rotor diatomic molecule, one can easily imagine that if the energy spacing between the quantum  $j$ -states were small compared to the width of the classical structure, that it might well be observable. This possibility was first considered in a comparison of classical differential cross sections for  $Li^+$  scattering from CO and  $N_2$  with experimental measurements[3]. In that study a number of rainbow-like

structures did appear in the rotational state distribution, and they were shown to be due to singularities in the Jacobian of eq. 6. These were called "rotational rainbows"[3] since the rainbow structure appeared in the rotational state distribution. Furthermore, the experimental time-of-flight spectra[40] also showed a number of anomalous peaks and shoulders which might have been noise but which qualitatively agreed with the classical results to a sufficient extent that it was conjectured that rotational rainbows were in fact experimentally observable. A number of experiments have now clearly demonstrated their existence[4-10].

### III. CLASSICAL ANALYSIS

In this section I give an extension of the classical analysis of  $\text{Li}^+ + \text{CO}$  scattering from CO begun in ref. 3. Since there has been some debate[14] over the terminology and interpretations different researchers in this area have used, I begin with a set of definitions of the various terms.

A rainbow is defined to be those points where the Jacobian in the classical cross section is singular. This definition includes the familiar rainbows of one-dimensional potential scattering as a special case. Following Ford and Wheeler[33], scattering in the neighborhood of a singular Jacobian will be referred to as rainbow scattering. When these singularities are observed in the rotational state distribution they will be called rotational rainbows. When observed in the angular distribution, they will be called angular rainbows or just rainbows. Arguments can no doubt be put forward in favor of not calling these

singularities rainbows at all. However, in the mathematical sense the singular Jacobian is a straightforward generalization of the one-dimensional case. Also, in the physical sense, it is shown below that when the Jacobian is singular, the scattering angle is always a constrained maximum or minimum. These analogies are, I believe, sufficiently strong to retain the rainbow terminology.

Also, I will distinguish between rainbow scattering and quantum mechanical interferences. Interferences occur any time there is more than one initial condition which leads to the same final state (e.g. the double slit experiment) and have nothing to do with rainbows per se. Adhering to the above definition of rainbow scattering, it is characterized by a sharp drop in the scattering intensity at the rainbow angle or j-value. This is a feature of both the classical and the quantum mechanical descriptions.

The center-of-mass coordinate system used to describe the scattering of an atom from a linear rigid rotor is shown in fig. 6.  $\vec{R}$ ,  $\vec{K}$  and  $\vec{J}$  are the relative position vector and linear and angular momentum vectors, respectively, of the atom and  $\vec{r}$ ,  $\vec{k}$  and  $\vec{j}$  are similarly defined for the rigid rotor. For a fixed value of the initial kinetic energy (constant K) and of the rotor's rotational energy (constant j), five initial values are necessary to uniquely define a trajectory. The complete differential cross section is given by[41],

$$\sigma(\theta, \phi, \alpha', \beta', j') = \sum_i \frac{b_i \sin \beta_i}{8\pi^2 \sin \beta' \sin \theta} \left| \frac{\partial(b_i, \chi_i, \alpha_i, \beta_i, \phi_i)}{\partial(\theta, \phi, \alpha', \beta', j')} \right| \quad (7)$$

$(b, \lambda)$  are the initial plane polar coordinates of the atom in the  $(x, z)$ -plane, and  $(\theta, \phi)$  are the final spherical polar coordinates of the scattered atom. Primes indicate final values. The sum over  $i$  is over all initial points  $(b, \lambda, \alpha, \beta, j')$  which lead to the same final point  $(\theta, \phi, \alpha', \beta', j')$ . Integrating over all final trajectory values except  $j'$  and  $\theta$  leads to the cross section formula, eq. 6.

In the examples that follow,  $j$ ,  $\alpha$  and  $\beta$  are fixed at zero corresponding to coplanar scattering with the rotor initially at rest. However, the analysis is valid for any initial  $j$ ,  $\alpha$  and  $\beta$ . The exact behavior of the rainbows when integrated over all  $\alpha$  and  $\beta$  remains a problem for future research.

The Jacobian in eq. 6 is made up of four partial derivatives,

$$\frac{\partial(b, r)}{\partial(j', \theta)} = \frac{\partial b}{\partial j'} \frac{\partial r}{\partial \theta} - \frac{\partial b}{\partial \theta} \frac{\partial r}{\partial j'} \quad (8)$$

It will be singular if any one of these derivatives is singular and at first glance there would appear to be four different types of singularities. Rather remarkably, however, all four derivatives are always simultaneously infinite. This means that one and only one type of rainbow is possible. A geometrical demonstration of this follows.

The rainbows can be located in the following way. Consider the two surfaces  $j'(b, r)$  and  $\theta(b, r)$ . Here and hereafter,  $j'$  is the angular momentum "quantum number" which is related to the classical angular momentum,  $j'_h$ , by,

$$j'_h = h \left( j' + \frac{1}{2} \right) \quad (9)$$

fig 7

All angles are given in degrees and lengths in Bohr radii.  $j'$  and  $\theta$  have been computed for  $\text{Li}^+\text{-CO}$  for the range  $3.6 < b < 7.0$  Bohr and  $0^\circ < \theta < 360^\circ$  at collision energy 4.28 eV. Stereographic projections of these two surfaces are shown in fig. 7. The classical functions  $j'$  and  $\theta$  can have both positive and negative values, but only their magnitudes are observable. Therefore, their absolute values have been plotted in fig. 7, resulting in cusps in both surfaces at  $j'$  and  $\theta$  equal zero. Experimental measurements[4] and a 3-dimensional classical trajectory calculation[13] have been done at this energy for scattering at  $\theta = 10^\circ$  for  $\text{Li}^+\text{-CO}$ , so let us consider the rotational state distribution at a fixed scattering angle of  $10^\circ$ . This defines a functional relationship between  $b$  and  $r$  which is shown by the dashed curve in fig. 8. This is a contour of constant  $\theta$ . The heavy black line on the  $j'$ -surface in fig. 7 is a trace of this constant- $\theta$  contour. The projection of this trace on the  $(j', r)$ -plane is the function whose slope gives the partial derivative  $\left(\frac{\partial r}{\partial j'}\right)_\theta$ . Likewise for the projection in the  $(j', b)$ -plane. Therefore, when  $j'$  reaches a local maximum on the constant- $\theta$  contour it must be a local maximum in the projections on both the  $(j', r)$ - and  $(j', b)$ -planes. As a result both of the partial derivatives  $\left(\frac{\partial r}{\partial j'}\right)_\theta$  and  $\left(\frac{\partial b}{\partial j'}\right)_\theta$  are infinite. This is shown in figs. 9(a) and 9(b) for the maximum at  $j'=12.17$ . Therefore, at each local extremum (both maxima and minima are possible) of  $j'$  on the constant- $\theta$  contour a rainbow will occur. Furthermore, this shows that at the rainbow,  $j'$  is a constrained extremum, the constraint being that  $\theta$  is constant.

fig 8

fig 9

We could now reverse the roles of  $j'$  and  $\theta$  in the above paragraph

and arrive at another set of rainbow points at which the other two partial derivatives were pair-wise singular. At each of these points  $\theta$  would be a constrained extremum with the constraint that  $j'$  is constant. In fact, however, the set of rainbow points found in this way would be identical to the set found in the above paragraph. That is, at each rainbow point ( $\theta, j'$ ), all four of the partial derivatives are singular. (This was first pointed out to me in discussions with J.L. Kinsey. Oversight of this led to an incorrect classification of rainbow types in ref. 3.) This can be demonstrated as follows.

We have already seen that at the rainbow point ( $\theta = 10.7, j' = 12.17$ ), two of the partial derivatives are singular. Let us now evaluate the other two. Fixing  $j' = 12.17$  defines a constant- $j'$  contour in the  $(b, \gamma)$ -plane. This is shown in fig. 8. The heavy black line on the  $\theta$ -surface in fig. 7 is a trace of this contour. Again, the partial derivatives can be evaluated from the projections of this trace on the  $(\theta, b)$ - and  $(\theta, \gamma)$ -planes. These projections are shown in figs. 9(c) and 9(d). It can be seen that on the constant- $j'$  contour  $\theta$  is also a local maximum at the rainbow point and hence the derivatives  $\frac{\partial \gamma}{\partial \theta}_{j'}$  and  $\frac{\partial b}{\partial \theta}_{j'}$  are singular. That this is generally true can be deduced from the fact that the constant- $\theta$  and constant- $j'$  contours are always tangent to one another at the rainbow points.

To reiterate, what has been shown is that there is one and only one type of rainbow and that it occurs at points where  $\theta$  and  $j'$  are simultaneously extrema, each subject to the constraint that the other is

held constant.

In the example given above, the scattering angle was  $10^\circ$ . All scattering at this and larger angles comes from trajectories of low impact parameter which hit the hard repulsive core of the CO molecule. Therefore, the occurrence of this rainbow in no way depends on the existence of an attractive well in the potential. This is in contrast to the one-dimensional case of simple potential scattering where there must be an attractive well to have a rainbow. Since the  $\text{Li}[\text{V}]-\text{CO}$  potential energy surface[42] does have a rather deep attractive well, the  $\phi$ -surface in fig. 7 does show at least two local unconstrained maxima to the left of the cusp. Intuitively, one feels that there must be some sort of different rainbow associated with those maxima. Indeed, something interesting does occur at those points.

Consider the contour of  $\phi = 7.3^\circ$  in the vicinity of  $b=6.0$  and  $r=80^\circ$  in fig. 10. There are two values of  $j'$  whose contours are tangent to the constant- $\phi$  contour, meaning that there are two rainbows of the type discussed above. These are at the points  $(\phi, j') = (7.3, 8.4)$  and  $(7.3, 25.97)$ . Now let us slowly raise the value of the  $\phi$ -contour and at each value find the two rainbow values of  $j'$ . This process will trace a "rainbow contour" in the  $(\phi, j')$ -plane, illustrated in fig. 11. At  $7.75^\circ$ , where  $\phi$  is an unconstrained maximum, the two rainbow points coalesce. Similar arguments will show that the same thing happens in the vicinity of a local unconstrained maximum in the  $j'$ -surface as well. As stated above, there is only one type of rainbow, but in the presence of

an attractive well, it is possible for two rainbows to coalesce. Other points of coalescence are also shown in fig. 11. Note that it is possible to distinguish between a confluence of rainbows at a maximum on the  $\theta$ -surface from one due to a confluence of rainbows at a maximum on the  $j'$ -surface. At a  $\theta$ -maximum the tangent of the rainbow contour is parallel to the  $j'$ -axis and at a  $j'$ -maximum the tangent is parallel to the  $\theta$ -axis. Only a section of the rainbow contour is shown in fig. 11. The complete rainbow contour would continuously connect all points of confluence, not all of which are necessarily shown in fig. 11.

An interesting research problem would be to relate the unconstrained maxima of the  $\theta$ - and  $j'$ -surfaces (at all orientations  $\alpha$  and  $\beta$ ) to a set of anisotropic parameters in the potential energy surface. Then, if experimental resolution were sufficient to locate the rainbow contours in the  $(\theta, j')$ -plane, these anisotropic parameters could be experimentally measured.

Double rainbows in the total differential cross sections have been observed in a number of calculations[43-46] and at least one experiment[47]. It can be seen in fig. 11 that if the differential cross sections were summed over all  $j'$ , the largest intensity would be at the two "coalescent" rainbow angles,  $\theta = 7.33^\circ$  and  $7.75^\circ$ . These are too close to be resolved in the experiment, but agree well with the observed rainbow angle at about  $7.5^\circ$ [4]. For a homonuclear diatomic molecule the  $\theta$ -surface is symmetric about  $\delta = 180^\circ$  and only one "coalescent" rainbow angle would be observed. Since CO varies only slightly from homonuclear

symmetry, the two angles are not widely separated. For highly unsymmetric heteronuclear diatomics, one could expect to observe a double rainbow in the total differential cross section. A similar argument is probably the correct explanation for why double rainbows appear in the scattering of Na from  $(CH)_3CX$  where  $X=Br, Cl$  and  $I$ , but only single rainbows are observed for  $(CH)_4C$ ,  $CBr_4$  and  $CCl_4$  [2,47]. The present analysis indicates that it is the asymmetry of the anisotropy and not just the anisotropy alone which produces multiple rainbows in the total differential cross sections. This was inferred by Buck, et. al. [47] from their measurements. In the case of heteronuclear diatomics another interesting research problem would be to try and relate the two "coalescent" rainbow angles to the two different collinear well depths.

An analogous effect occurs in the integral cross sections, integrated over all scattering angles. Fig. 11 predicts peaks in the rotational state distribution at the "coalescent"  $j$ -values of about  $j'=7, 13, 18$  and  $31$ .

#### IV. REVIEW

##### A. Theory

In addition to ref. 3, three other studies of  $Li^+-CO$  have been done [11,13,42]. In ref. 11 classical partial cross sections (fixed impact parameter) were compared with the coupled states approximation [48,49]. More recently, classical calculations were done [13] for scattering angle  $10^\circ$  and collision energy,  $E=4.28$  eV. to

compare with time-of-flight (TOF) measurements[4] which clearly show structure in the rotational state distribution. This comparison is noteworthy in the following respect. Using Gaussian line widths which account for the finite resolution of the experimental apparatus, the TOF spectrum was calculated from the classical cross sections. The two calculated classical rotational rainbows were effectively washed out by the line broadening of the apparatus. In contrast the experiment showed four distinct, well resolved peaks. Barring an unforeseen drastic change in the classical results due to improvements in the potential energy surface, it would appear that quantum mechanical interferences are necessary to explain the observed structure. If true, this is in remarkable contrast to the commonly held belief that when the collision energy is large compared to the quantum state energy spacings, most interference effects are quenched and a classical description is valid. A semiclassical analogue of the treatment in the previous section is in progress[50] which may shed further light on this.

Schepper et. al. [5,15] have modeled high angle scattering of K from CO and ~~N<sub>2</sub>~~ with collisions from a hard ellipsoid. The full, 3-dimensional classical analysis of this model problem can be carried out exactly and they find good agreement with their measurements. They have called the structure "bulge singularities" or the "bulge effect" alluding to the topology of the ellipsoid.

Another approximation which can be used to study rotational rainbows is the quantum mechanical IOS approximation. (For a review and extensive

references to the original IOS literature see ref. 51.) In this approximation explicit averaging over the  $\alpha$  and  $\beta$  orientation angles is eliminated so that only the impact parameter (or equivalently the orbital angular momentum) and the initial molecular orientation angle remain. A correct semiclassical analysis of this approximation results in a cross section formula which contains a Jacobian, equivalent to that in eq. 6 [20,23]. Although the IOS approximation is no doubt more accurate than the coplanar approximation in most cases, the location and interpretation of the rainbow structures in this formalism do not differ in any significant respect from that in the coplanar classical description. Schinke and various co-workers have used the IOS approximation to study  $\text{Li}^+/\text{H}_2$  [16],  $\text{K}-\text{Na}$ ,  $\text{K}-\text{CO}$  [18] and  $\text{He}-\text{Na}_2$  [17,22] collisions.

Bowman[23] and Schinke[16], however, have both made an approximation beyond the IOS and semiclassical approximations, arriving at cross section formulas which contain a simple product of two partial derivatives rather than a 2x2 Jacobian. Instead of locating the singularities of the Jacobian, eq. (8), one can equivalently locate the zeros of its inverse,

$$\frac{\partial(j', \theta)}{\partial(b, \delta)} = \left( \frac{\partial j'}{\partial b} \right)_\delta \left( \frac{\partial \theta}{\partial \delta} \right)_b - \left( \frac{\partial j'}{\partial \delta} \right)_b \left( \frac{\partial \theta}{\partial b} \right)_\delta \quad (10)$$

In general, when this Jacobian is zero, none of its four partial derivatives is zero. Therefore, the physical interpretation of the rainbow, that is the extremal nature of  $j'$  and  $\theta$ , is somewhat

obscured. At large scattering angles for some systems (see, for example, ref. 20, fig. 4) the constant  $\theta$ -contours in the  $(b, \gamma)$ -plane are nearly parallel to the  $\gamma$ -axis. It follows in this case that,

$$\left. \frac{\partial \theta}{\partial \gamma} \right|_b \approx 0 \quad (11)$$

and

$$\frac{\partial(j', \theta)}{\partial(b, \gamma)} \approx - \left. \frac{\partial j'}{\partial \gamma} \right|_b \left. \frac{\partial \theta}{\partial b} \right|_\gamma \quad (12)$$

Bowman acknowledges that a complete, 2-dimensional, stationary phase approximation to the IOS formula contains a 2x2 Jacobian similar to eq. (10). He used the simpler formula, eq. (12), in his analysis[23], however, since for the system he was studying this was a good approximation. In Schinke's stationary phase analysis of the IOS approximation[16], he independently derived a formula similar to Bowman's. In his derivation the approximation, eq. (12), is implicit and unstated. Much of Schinke's later analysis[17,18,21] also depends on this approximation.

While the approximation, eq. (12), is in some cases valid one should exercise caution in basing physical interpretations on it. For example, eq. (12) has been interpreted[10,17,18,23] to mean that there are two types of rainbows - a normal or "impact parameter" type due to the zeros of  $\left. \frac{\partial \theta}{\partial b} \right|_\gamma$  and an "orientation angle" type due to the zeros of  $\left. \frac{\partial j'}{\partial \gamma} \right|_b$ . Based on this interpretation, Serri et. al. [10] have proposed the term "halo" - an appropriate analogy only if eq. (12) were exact rather than

approximate. Schinke has interpreted eq. (11) to mean that interfering trajectories near a rainbow differ only in their initial orientation angle,  $\chi$ , and has used the term "orientation-interference oscillations"[16]. In general, however, the interfering trajectories have different impact parameters as well. This is easily seen in the constant- $\theta$  contours in fig. 8 of the previous section, fig. 9 of ref. 3 and fig. 4 of ref. 20.

With the exception of one partial cross section calculation for He-CO collisions[12], no discussion of rotational rainbows has been given in the context of exact quantum mechanical calculations. It is entirely possible that rainbow structures may be present in some previous close coupling calculations and have simply gone unnoticed. However, the conditions for most clearly observing them - high energy and large rotational transitions - result in too many open channels for converged close coupling calculations. With new improvements to close coupling methods [12,52], there is hope that some such studies can be undertaken in the near future.

## B. Experiment

The experimental study of rainbows in inelastic collisions is also receiving an increasing amount of attention. Eastes et. al. [4] have measured TOF spectra for  $\text{Li}^+ - \text{CO}$  collisions at scattering angles  $3^\circ - 13^\circ$  and collision energy 4.28 eV. They clearly resolve a number of peaks in the rotational state distribution.

Beck and co-workers have measured energy loss spectra for K scattering from CO and  $N_2$  [5], for scattering angles greater than  $90^\circ$  and energies 0.34-1.24 eV. and have also observed an isotope effect in the observed structure [6]. They have successfully modeled their results with classical scattering from a hard ellipsoid [5,15].

Bergmann and co-workers have done a number of experiments with He [7,8] and Ne [9] collisions with  $Na_2$  using spectroscopic observation techniques. They observe rainbow structure in both the rotational state and angular distributions. Serri et. al. [10] have reported structure in similar measurements for Ar- $Na_2$  collisions.

#### Acknowledgement

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## References

- [ 1] R.B.Bernstein, Quantum effects in elastic molecular scattering,  
Advan. Chem. Phys. 10: 75 (1966)
- [ 2] U.Buck, Elastic scattering,  
Advan. Chem. Phys. 30: 313 (1975)
- [ 3] L.D.Thomas, Classical trajectory study of differential cross  
sections for  $\text{Li}^+\text{-CO}$  and  $\text{N}_2$  inelastic collisions,  
J. Chem. Phys. 67: 5224 (1977)
- [ 4] W.Eastes, U.Ross and J.P.Toennies, Experimental observation of  
structure in the distribution of final rotational states in small  
angle inelastic scattering of  $\text{Li}^+$  from CO (E.c.m.=4-7 eV),  
Chem. Phys. 39: 407 (1979)
- [ 5] W.Schepper, U.Ross and D.Beck, Anisotropy of the repulsive  
intermolecular potential from rotationally inelastic scattering,  
Z. Phys. A 290: 131 (1979)
- [ 6] D.Beck, U.Ross and W.Schepper, Isotope shift in the bulge effect of  
molecular scattering,  
Phys. Rev. A 19: 2173 (1979)
- [ 7] K.Bergmann, R.Engelhardt, U.Hefter and J.Witt, State-to-state  
differential cross sections for rotational transitions in  $\text{Na} + \text{He}$   
collisions,  
J. Chem. Phys. 71: 2726 (1979)
- [ 8] K.Bergmann, U.Hefter and J.Witt, State-to-state differential cross  
sections for rotationally inelastic scattering of  $\text{Na}$  by He,  
J. Chem. Phys. 72: 4777 (1980)
- [ 9] K.Bergmann, U.Hefter, A.Mattheus and J.Witt, Resolution of angular  
rotational rainbows in  $\text{Na} - \text{Ne}$  collisions,  
preprint (March, 1980)
- [10] J.A.Serri, A.Morales, W.Moskowitz, D.E.Pritchard, C.H.Becker and  
J.L.Kinsey, Observation of halos in rotationally inelastic  
scattering of  $\text{Na}$  from Ar,  
J. Chem. Phys. 72: 6304 (1980)
- [11] L.D.Thomas, W.P.Kraemer, G.H.F.Diercksen and P.McGuire, Comparison  
of classical mechanics and the coupled states approximation for  
 $\text{Li}^+\text{-CO}$  scattering on an ab initio calculated CI potential energy  
surface,  
Chem. Phys. 27: 237 (1978)

- [12] L.D.Thomas, Solution of the coupled equations of inelastic atom-molecule scattering for a single initial state, J. Chem. Phys. 70: 2979 (1979)
- [13] L.D.Thomas, W.P.Kraemer and G.F.H.Diercksen, Low angle scattering of  $\text{Li}^+ + \text{CO}$ , Chem. Phys. Lett. (accepted for publication, July 1980)
- [14] L.D.Thomas, On rainbow scattering in inelastic molecular collisions, J. Chem. Phys. (accepted for publication in the 1 December 1980 issue)
- [15] D.Beck, U.Ross and W.Schepper, Rotationally inelastic classical scattering from an anisotropic rigid shell potential of rotation symmetry, Z. Phys. A 293: 107 (1979)
- [16] R.Schinke, Theoretical studies of vib-rotational excitation in  $\text{Li}^+ + \text{H}_2$  collisions at intermediate energies, Chem. Phys. 34: 65 (1978)
- [17] R.Schinke and P.McGuire, Rotational rainbow oscillations in  $\text{He}-\text{Na}_2$  collisions: comparison between coupled states and infinite order sudden approximations, J. Chem. Phys. 71: 4201 (1979)
- [18] R.Schinke, Quantum effects in rotationally inelastic molecular scattering:  $\text{K} + \text{N}_2$  and  $\text{K} + \text{CO}$  collisions on simple model surfaces, J. Chem. Phys. 72: 1120 (1980)
- [19] R.Schinke, Rotational rainbow maxima: a time dependent study, Chem. Phys. 47: 287 (1980)
- [20] H.J.Korsch and R.Schinke, A uniform semiclassical sudden approximation for rotationally inelastic scattering, J. Chem. Phys. 73: 1222 (1980)
- [21] R.Schinke, Inversion of rotationally inelastic differential cross sections under sudden conditions, J. Chem. Phys. (submitted for publication)
- [22] R.Schinke, W.Müller, W.Meyer and P.McGuire, Theoretical investigation of rotational rainbow structures in  $\text{X} - \text{Na}_2$  collisions using CI potential surfaces. I. rigid-rotor  $\text{X}=\text{He}$  scattering and comparison with state-to-state experiments, J. Chem. Phys. (submitted for publication)
- [23] J.M.Bowman, Rotational rainbows in inelastic atom-molecule differential cross sections, Chem. Phys. Lett. 62: 309 (1979)

- [24] C.B.Boyer, "The rainbow from myth to mathematics", Thomas Yoseloff, New York (1959)
- [25] L.W.Taylor, "Physics: the pioneer science", Houghton Mifflin Co., the Riverside Press, Cambridge (1941), p. 498-503
- [26] Descartes, "Les Meteores" (1637), see english translation in, W.F.Magie, "A source book in physics", McGraw-Hill, New York (1935), p. 273
- [27] Ref. [25], p. 406
- [28] I.Newton, "Opticks: or a treatise of the reflections, refractions, inflections and colours of light", 3rd edition, London (1721) p. 147
- [29] G.B.Airy, On the intensity of light in the neighbourhood of a caustic, Trans. Camb. Phil. Soc. 6: 379 (1838)
- [30] A.Sommerfeld, "Optics", Academic Press, New York (1954) p. 352
- [31] R.Mecke, Andere Fälle von Beugung, Chapter 3 in: "Handbuch der Physik", Vol. 20, H.Konen ed., Springer, Berlin (1928) p. 67
- [32] H.Goldstein, "Classical mechanics", Addison-Wesley, Reading, Mass. (1950) p. 82
- [33] K.W.Ford and J.A.Wheeler, Semiclassical description of scattering, Ann. Phys. 7: 259 (1959)
- [34] F.A.Morse, R.B.Bernstein and H.U.Hostettler, Evaluation of the intermolecular potential well depth from observations of rainbow scattering: Cs-Hg and K-Hg, J. Chem. Phys 36: 1947 (1962)
- [35] U.Buck and H.Pauly, Determination of intermolecular potentials by the inversion of molecular beam scattering data. II. high resolution measurements of differential scattering cross sections and the inversion of the data for Na-Hg, J. Chem. Phys. 54: 1929 (1971)
- [36] W.H.Miller, Semiclassical theory of atom-diatom collisions: path integrals and the classical S matrix, J. Chem. Phys. 53: 1949 (1970)
- [37] J.N.L.Connor and R.A.Marcus, Theory of semiclassical transition probabilities for inelastic and reactive collisions. II. asymptotic evaluation of the S matrix, J. Chem. Phys. 55: 5636 (1971)

- [38] W.H.Miller, The classical S-matrix in molecular collisions,  
Advan. Chem. Phys. 30: 77 (1975)
- [39] W.R.Gentry, Ion-dipole scattering in classical perturbation theory,  
J. Chem. Phys. 60: 2547 (1974)
- [40] R.Böttner, U.Ross and J.P.Toennies, Measurements of rotational and  
vibrational quantum transition probabilities in the scattering of  
Li<sup>+</sup> from N<sub>2</sub> and CO at center of mass energies of 4.23 and 7.07  
eV.,  
J. Chem. Phys. 65: 733 (1976)
- [41] L.D.Thomas, The calculation of classical transition probabilities in  
atom-molecule collisions for fixed total angular momentum,  
Chem. Phys. Lett. 51: 35 (1977)
- [42] L.D.Thomas, W.P.Kraemer and G.H.F.Diercksen, Classical trajectory  
study on an ab initio CI vibrator potential energy surface for  
Li<sup>+</sup>-CO differential cross sections,  
Chem. Phys. 30: 33 (1978)
- [43] R.J.Cross, Jr., Classical small-angle scattering from anisotropic  
potentials,  
J. Chem. Phys. 46: 609 (1967)
- [44] R.M.Harris and J.F.Wilson, Optical model analysis of nonreactive  
collisions of reactive molecules: scattering of K, Rb, and Cs from  
CCl<sub>4</sub>, CH<sub>3</sub>I, and SnCl<sub>4</sub>,  
J. Chem. Phys. 54: 2088 (1971)
- [45] U.Buck and V.Khare, A comparison of different sudden approximations  
for molecular scattering,  
Chem. Phys. 26: 215 (1977)
- [46] F.E.Budenholzer and E.A.Gislason, Classical differential cross  
sections for anisotropic potentials,  
J. Chem. Phys. 68: 4222 (1978)
- [47] U.Buck, F.Gestermann and H.Pauly, Double rainbows in atom-molecule  
scattering,  
Chem. Phys. Lett. 33: 186 (1975)
- [48] P.McGuire and D.J.Kouri, Quantum mechanical close coupling approach  
to molecular collisions. j<sub>z</sub>-conserving coupled states approximation,  
J. Chem. Phys. 60: 2488 (1974)
- [49] R. T Pack, Space-fixed vs body-fixed axes in atom-diatomic molecule  
scattering. Sudden approximations.  
J. Chem. Phys. 60: 633 (1974)

- [50] G.E.Zahr and L.D.Thomas, Semiclassical calculation of rotational rainbows in coplanar  $\text{Li}^+\text{N}_2\text{-CO}$  collisions, (to be published)
- [51] R.Goldflam, S.Green and D.J.Kouri, Infinite order sudden approximation for rotational energy transfer in gaseous mixtures, J. Chem. Phys. 67: 4149 (1977)
- [52] L.D.Thomas, Iterative method for a single column of the S-matrix using a matrix Green function, (to be published)

# Figure captions

- Fig. 1 (a) Path of light ray through a water drop at the rainbow deflection angle  $\theta = 137.92^\circ$ . (b) Impact parameter vs. deflection angle. (c) Derivative of the lower single-valued branch of the impact parameter vs. the deflection angle.
- Fig. 2 Intensity of light scattered from a water drop as predicted by geometrical optics and Airy's formula for wave optics (redrawn from ref. 29.)
- Fig. 3 (a) Trajectories of two colliding atoms in the center-of-mass frame. (b) The impact parameter as a function of the deflection angle. (c) Schematic of the scattering cross section according to classical (solid line) and semiclassical mechanics (dashed line.)
- Fig. 4 (a) Example of rainbow scattering (observations corrected to the c.m. system. K-Hg,  $v = 1026 \text{ m/sec}$ ). (b) Alternate representation of the same data. (Reprinted with permission from ref. 34., fig. 1)
- Fig. 5 Measured differential cross sections for NaHg of five different energies in the center of mass system. Supernumerary rainbows are well resolved. (Reprinted with permission from ref. 35., fig. 7)
- Fig. 6 Coordinates used to define the initial values of a trajectory.
- Fig. 7 Stereographic projections of the surfaces  $j'(b, \gamma)$  (upper figure) and  $\theta(b, \gamma)$  (lower figure.) The heavy black line on the upper surface is a trace of the contour  $\theta = 10^\circ$ . Projections of this trace are shown in the  $(j', b)$ - and  $(j', \gamma)$ -planes. The heavy black lines on the lower surface are the trace of the contour  $j' = 12.17$ . Projections of this trace are shown in the  $(\theta, b)$ - and  $(\theta, \gamma)$ -planes. Focusing the right eye on the right figure and the left eye on the left figure will produce a 3-D image. Placing a long letter-size envelope on edge between the left and right figures is a useful visual aid.
- Fig. 8 Contours of constant  $\theta = 10^\circ$  (dashed) and constant  $j' = 12.17$  (solid) in the  $(b, \gamma)$ -plane.
- Fig. 9 (a)  $b(j', \theta)$  for constant  $\theta = 10^\circ$ . (b)  $\gamma(j', \theta)$  for constant  $\theta = 10^\circ$ . (c)  $b(j', \theta)$  for constant  $j' = 12.17$ . (d)  $\gamma(j', \theta)$  for constant  $j' = 12.17$ .
- Fig. 10 Contours of constant  $\theta$  (dashed) and constant  $j'$  (solid).
- Fig. 11 Points in the  $(j', \theta)$ -plane where two or more rainbows coalesce. Solid circles - points due to local maxima on the

surface  $j'(b, \gamma)$ . Open circles - points due to local maxima on the surface  $\Phi(b, \gamma)$ . The solid line is a segment of the "rainbow contour".

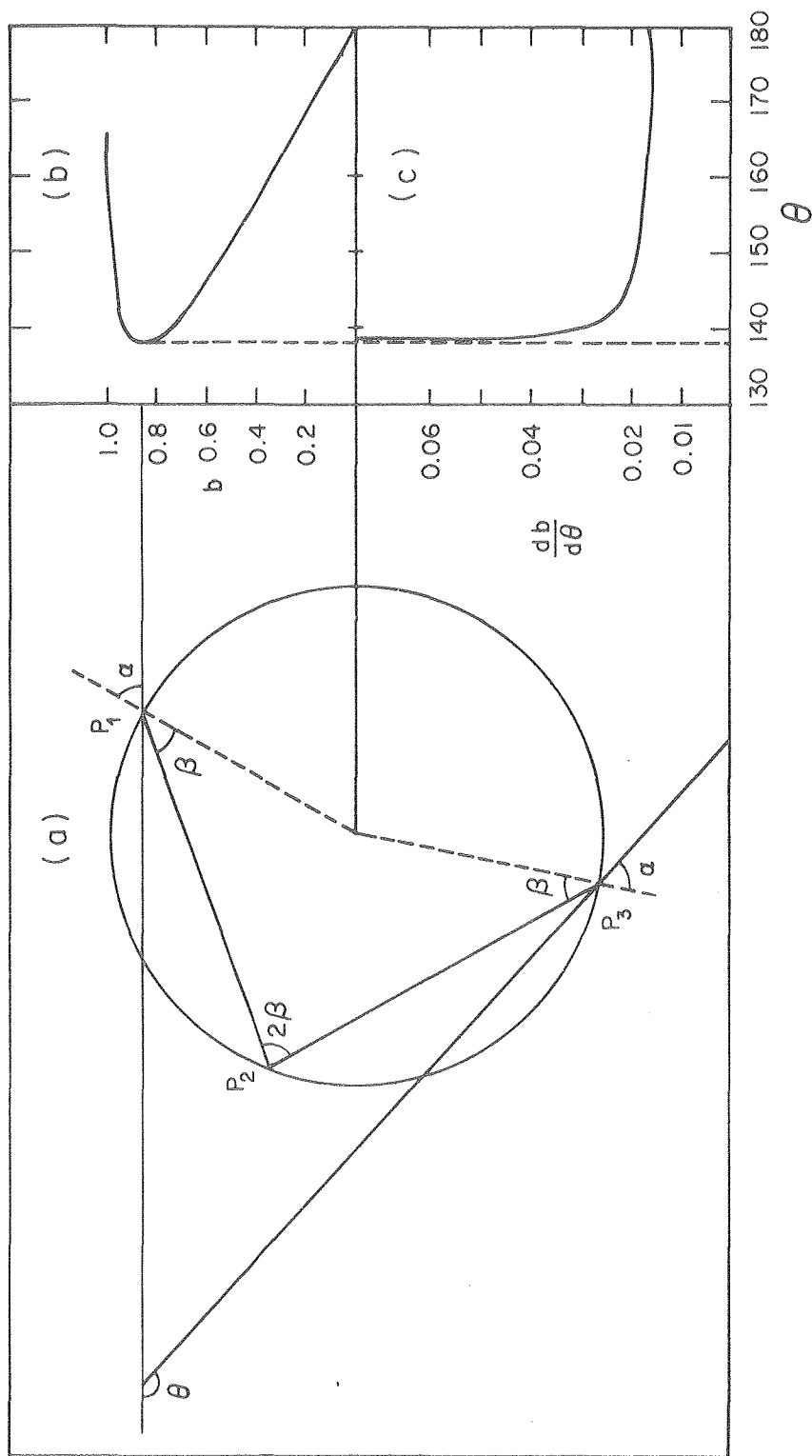


Fig. 1

XBL808-1808

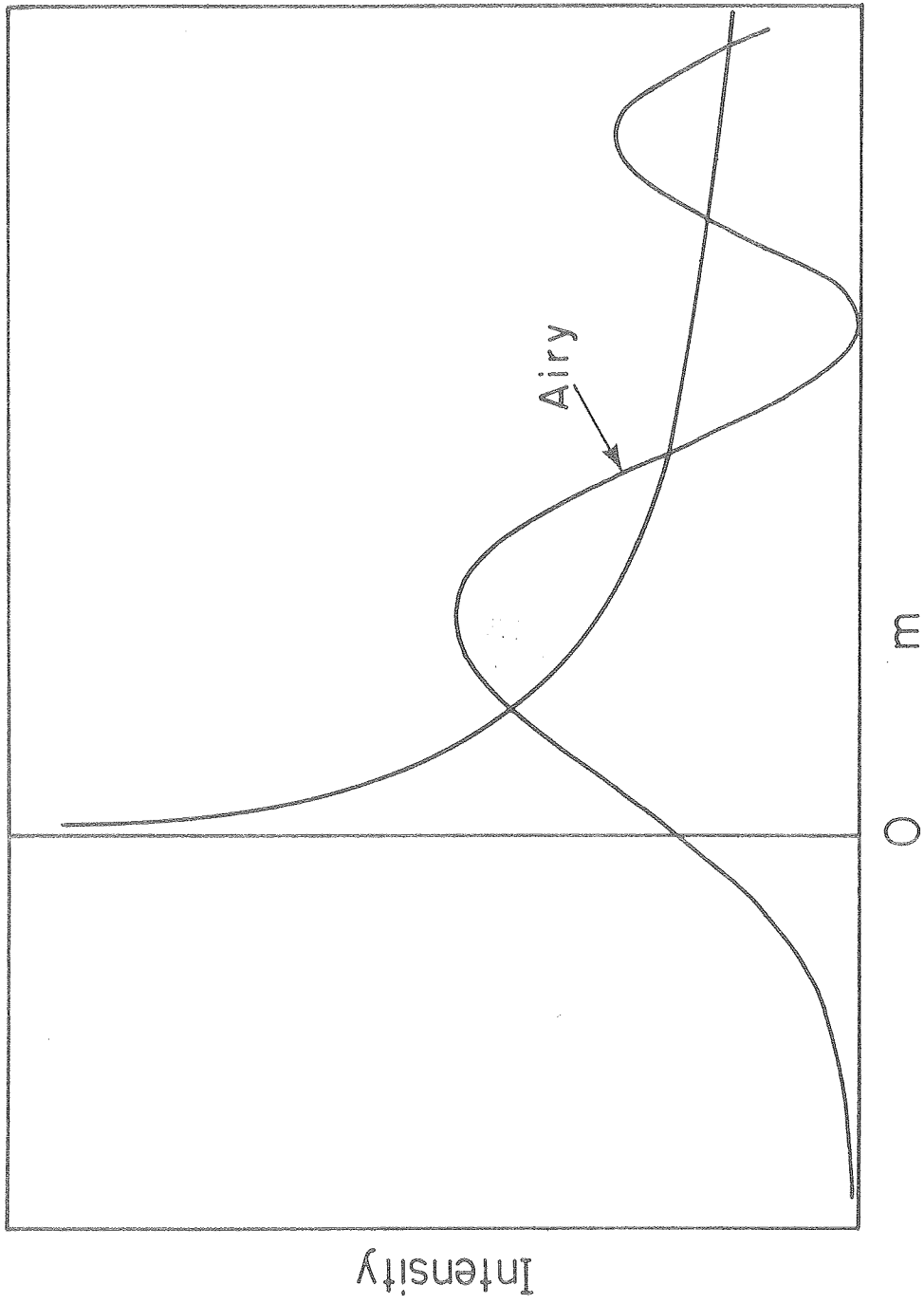


Fig. 2

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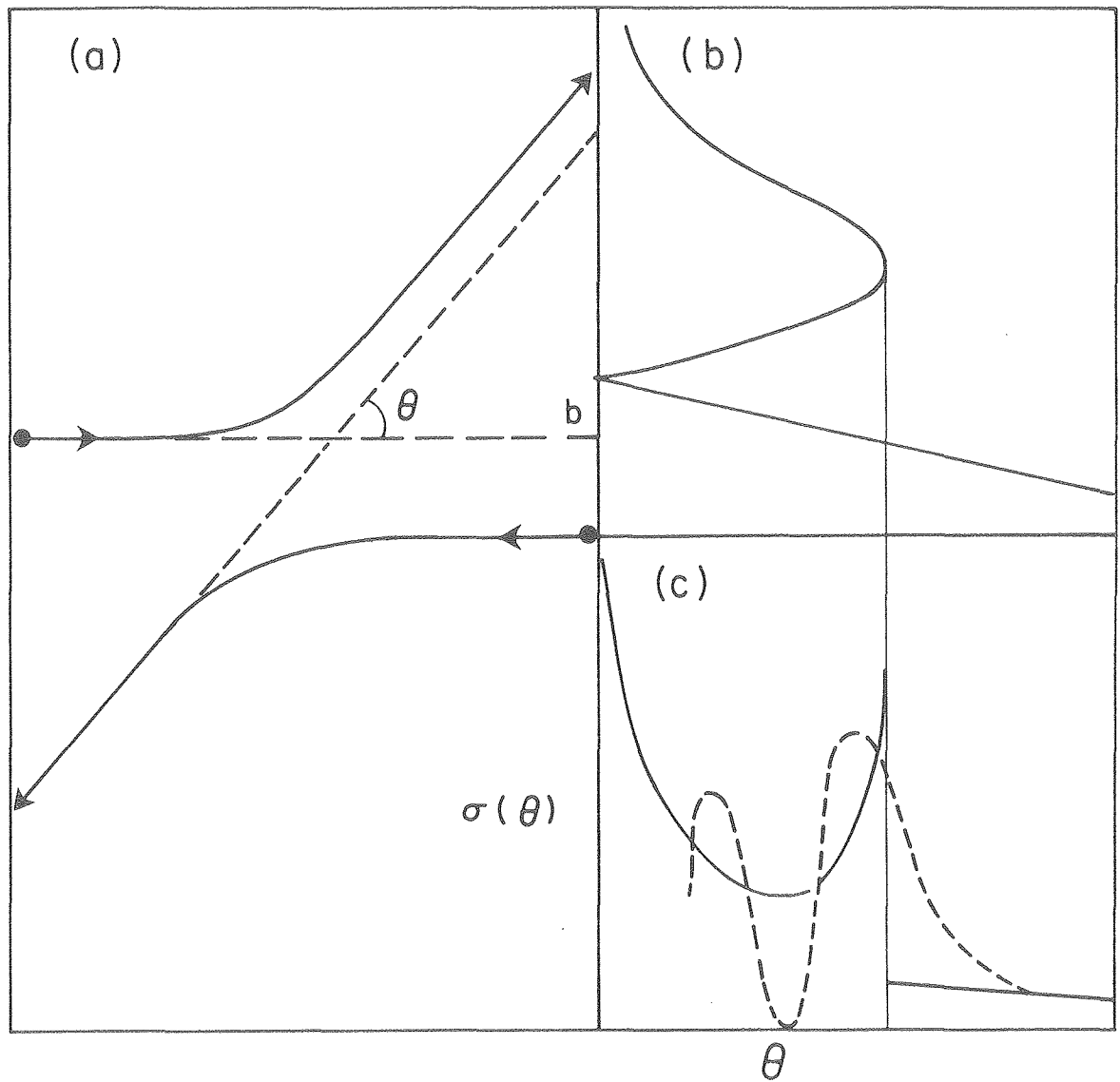


Fig. 3

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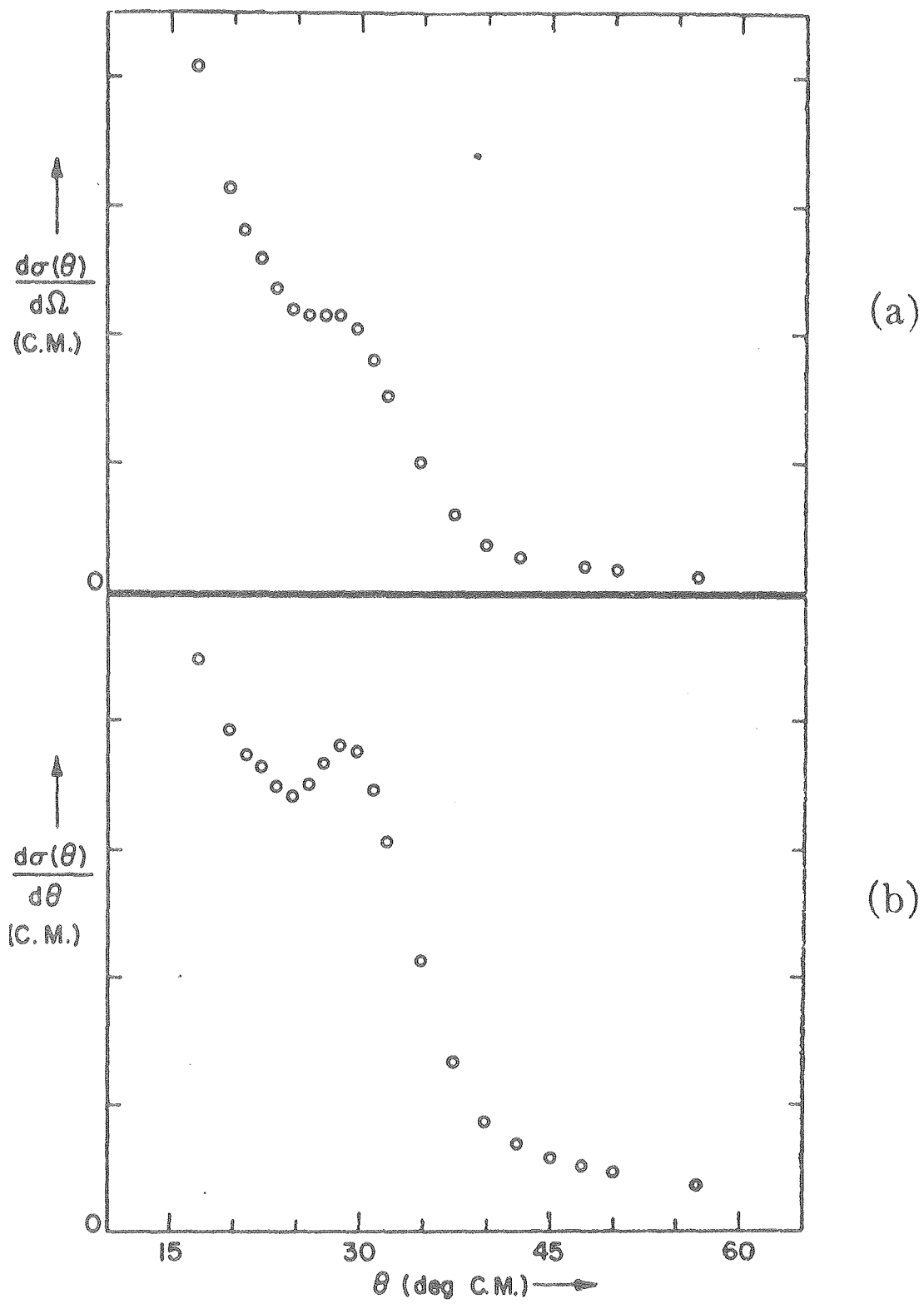


Fig. 4

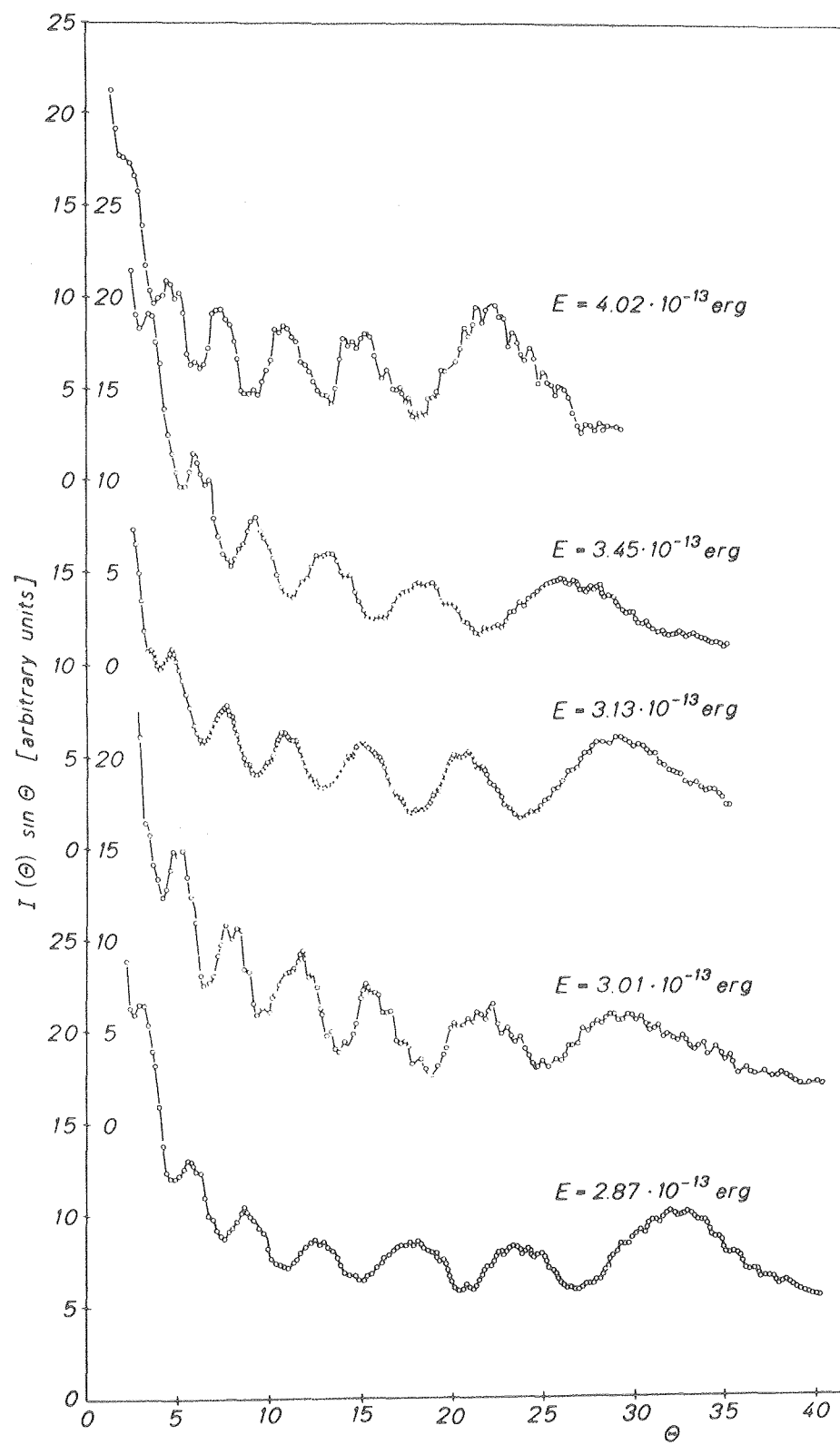


Fig. 5

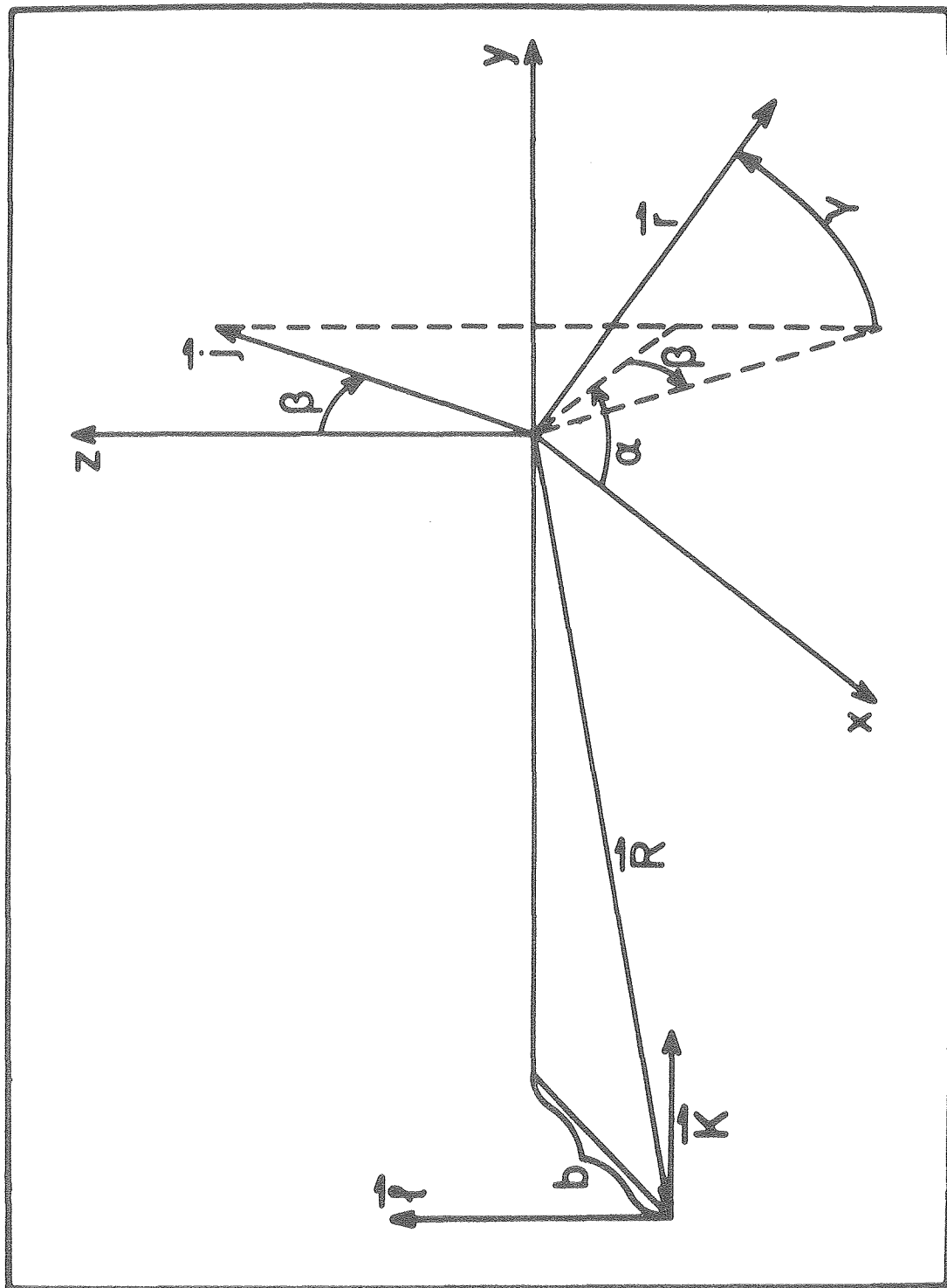


Fig. 6

XBL 808-11341

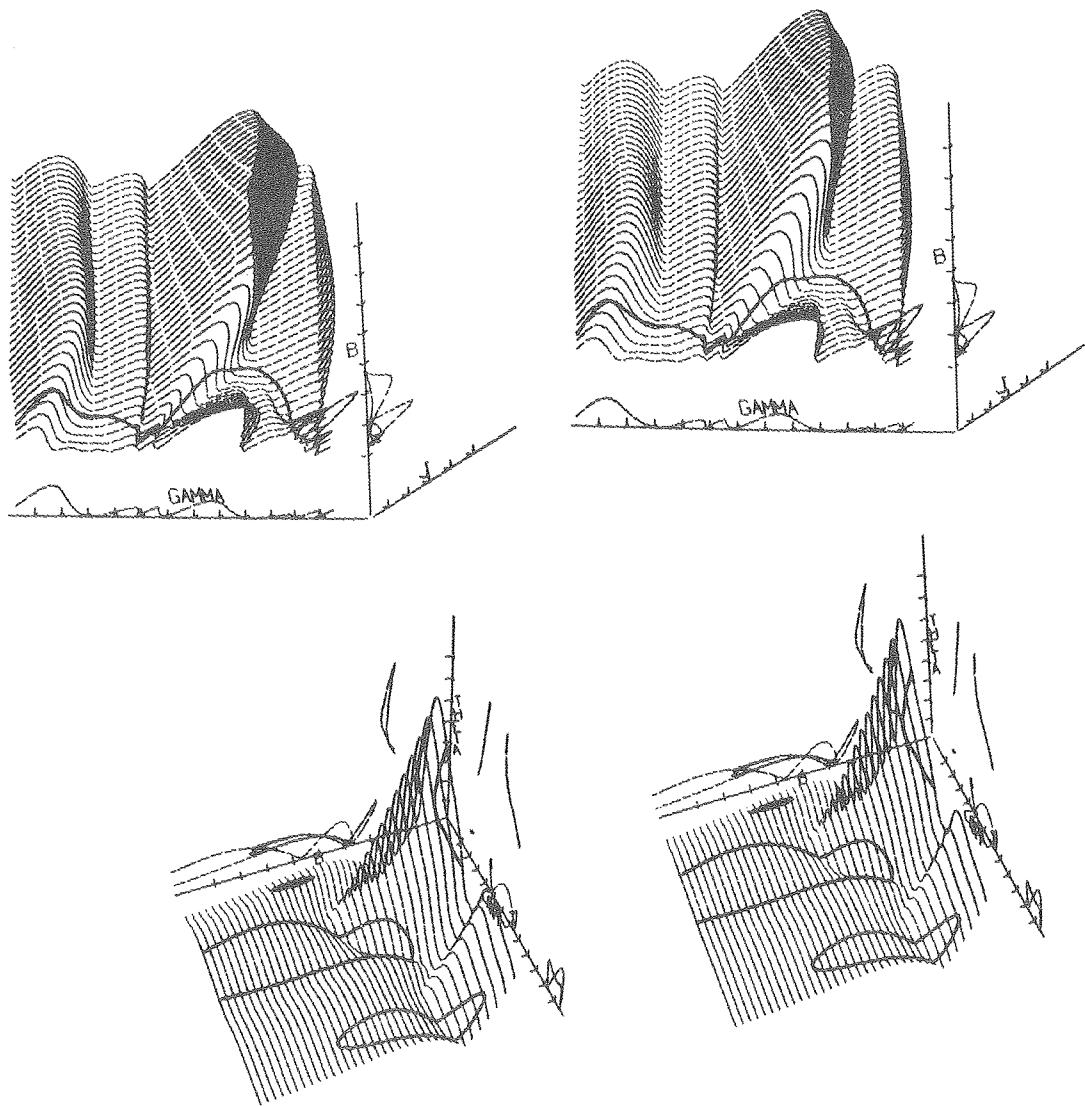


Fig. 7

XBL 808-11214

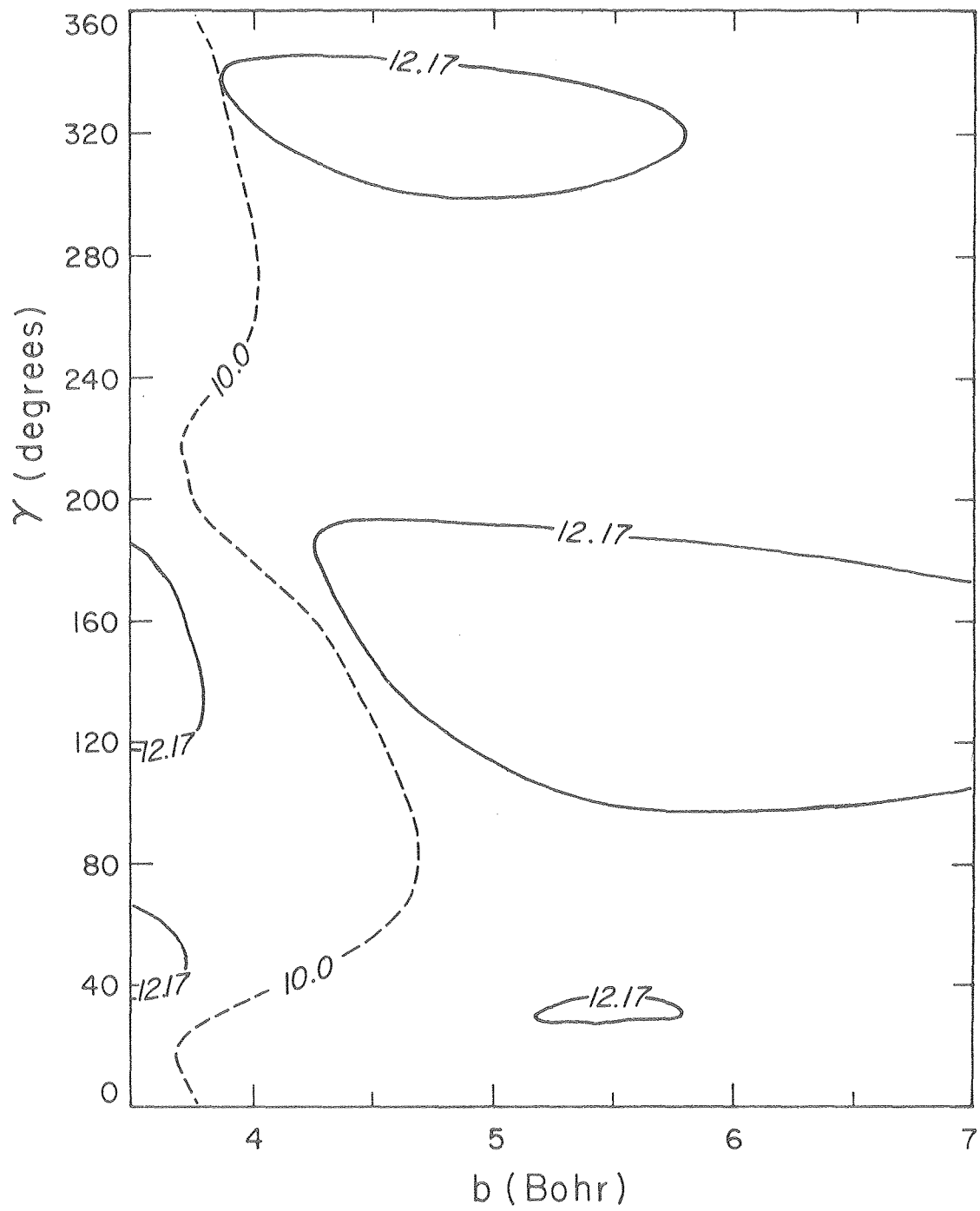


Fig. 8

XBL808-1807

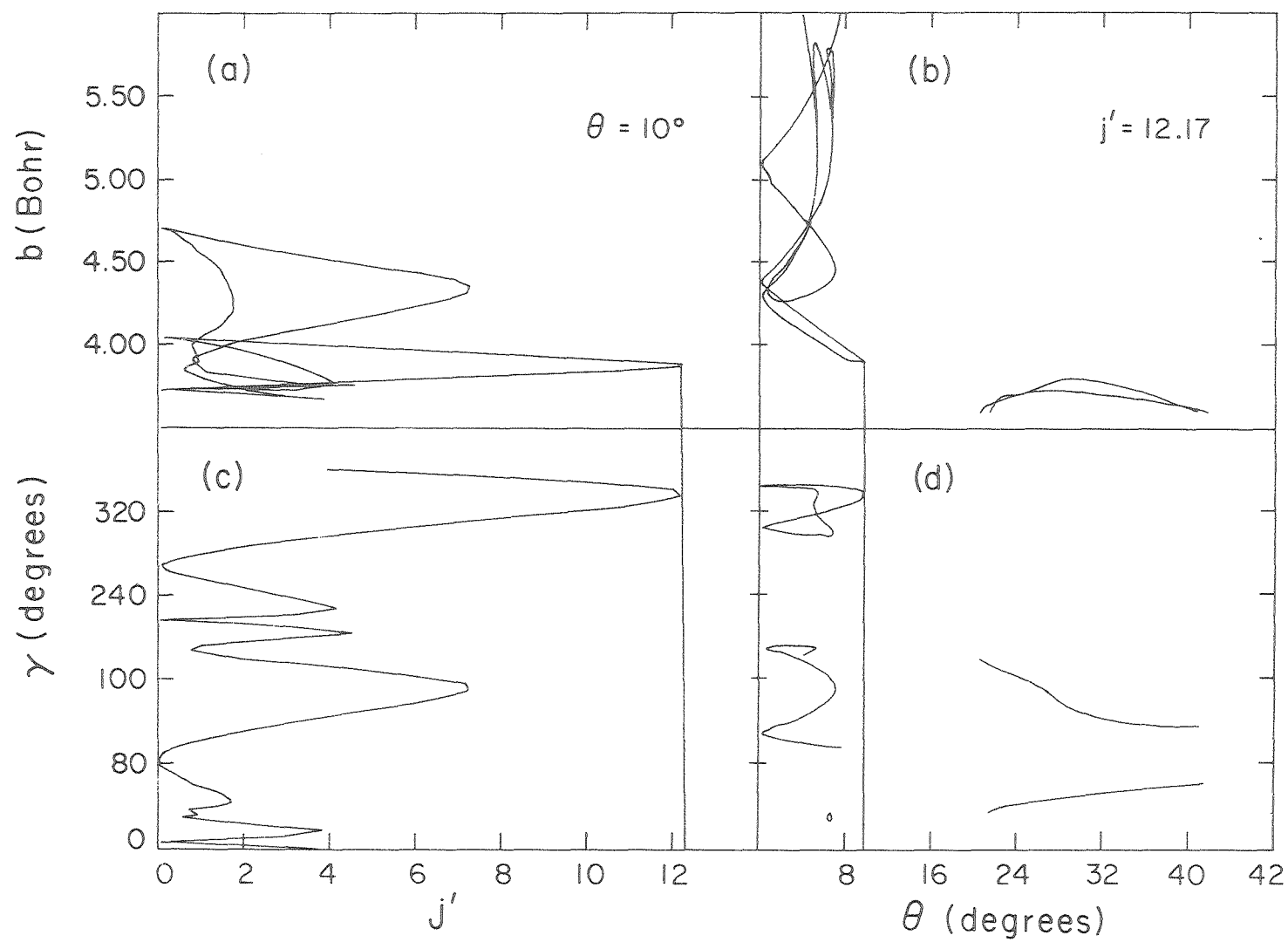


Fig. 9

XBL808-1803

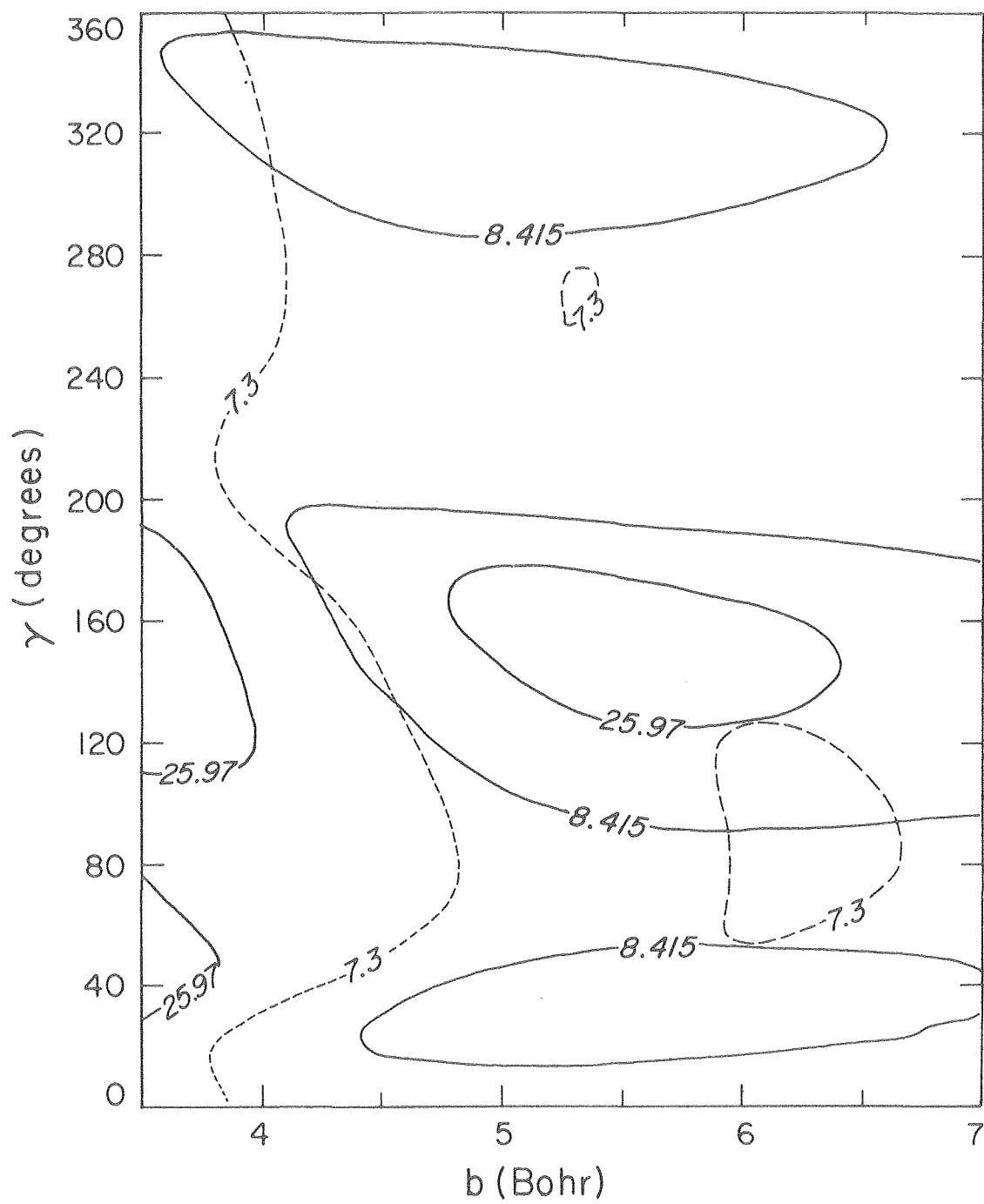


Fig. 10

XBL 808-1806

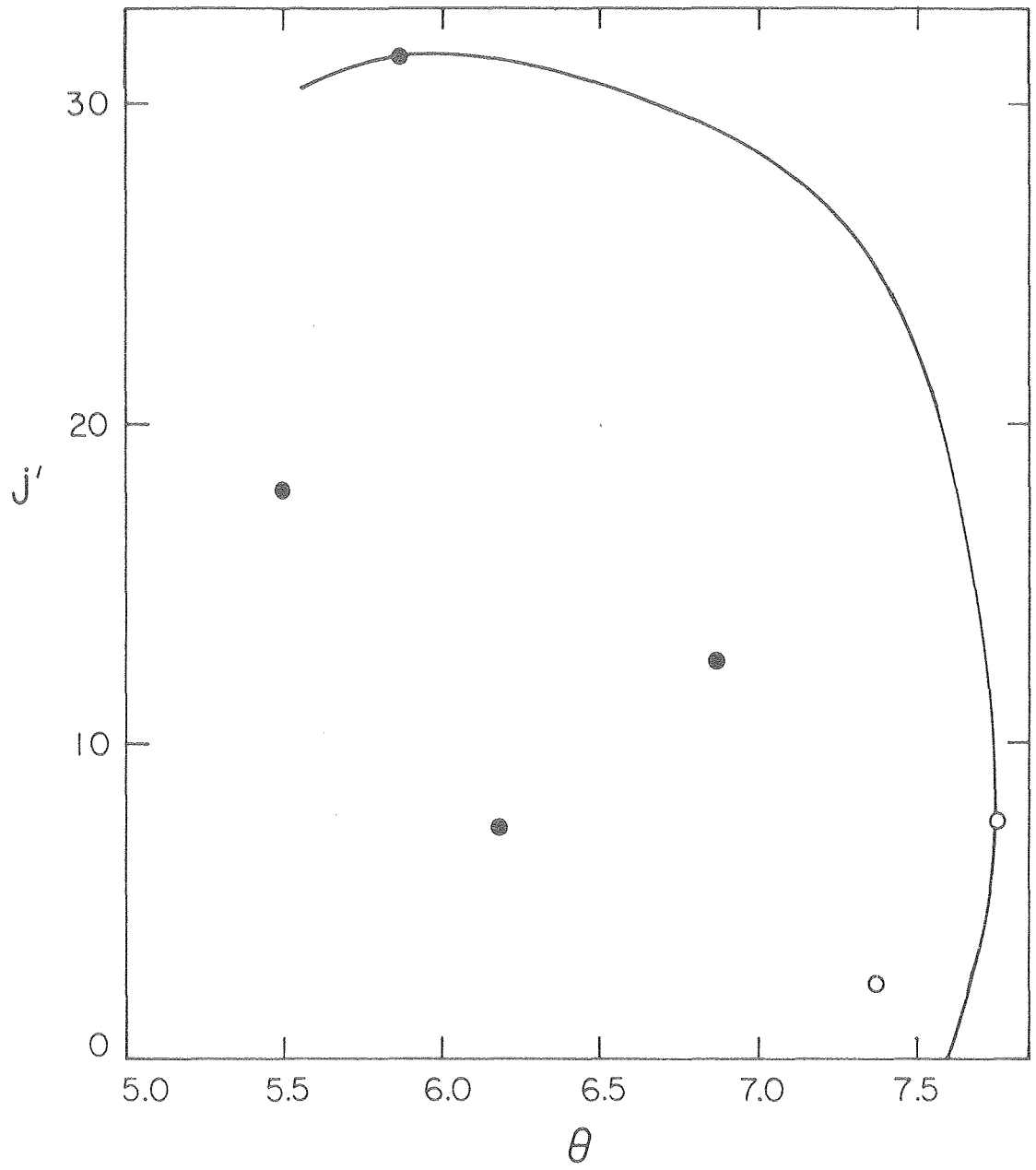


Fig. 11

XBL 808-1805

